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OPTICAL FILMS FOR SOLAR ENERGY APPLICATIONS

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Abstract

A number of solar energy conversion materials and coatings are considered stratified media. They are generally classified as graded-index media or layered media. With index coatings, two components (such as air and SiO_2 or Cr and Cr_2O_3) are created in a non-linear fashion with depth into the coating. By simple materials admixing, a coating is formed with varying optical constants (n , k). Layered media generally consist of interference films, films with thicknesses below the wavelength of light, made of alternating dissimilar media such as a dielectric and metal combination. This paper presents details of the properties of stratified coatings. Coatings that serve as antireflection films, transparent optical insulation (silica aerogel), thermal heat mirrors, or selective absorbers are also discussed. Both interference and semiconductor types of heat mirrors are evaluated. Four types of selective absorbers are also covered: dendritic optical trapping, graded composite, metal/dielectric tandems, and optical interference techniques.

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Introduction

Stratified optical materials and coatings play an important role in improving the efficiency of solar conversion processes. At present the best-known stratified media are multilayer and graded-index films. Stratified media are used as heat mirrors, selective absorbers, antireflective films, and transparent insulation. Graded-index films can be homogenous materials, spatially oriented structures, or etched materials. Such films and materials improve efficiency and allow for innovation in energy-efficient windows, passive and active energy conversion, and photovoltaics. The horizons of invention can be expanded by considering new materials, techniques, and concepts that can increase the efficiency of energy utilization in buildings and transform solar energy into heat, light and electrical power. The stability requirements for materials to effectively collect and transmit solar energy are extremely demanding. This, combined with the need for inexpensive production methods, creates a broad area for innovative scientific research. We describe several approaches and materials systems for two broad application categories: 1) low-conductance, high-transmittance systems and 2) solar absorbers.

Low-Conductance, high-transmittance materials

Heat-mirror coatings

Heat-mirror coatings play a significant role as transparent insulation for architectural windows¹ and in solar thermal^{2,3} and photovoltaic conversion. In this work a heat mirror is defined as a coating that is predominately transparent over the visible wavelengths (0.30 - 0.77 microns) and reflective in the infrared (2.0 - 100 microns). Over the near-infrared (0.77 - 2.0 microns) the coating may exhibit combined properties depending on design or application. Figure 1 shows an idealized heat-mirror response superimposed on solar and blackbody radiation spectra. Heat mirrors for windows derive their usefulness from their low emittance (typically 0.05 - 0.2) or high reflectance in the infrared. The lower the emittance, the less the magnitude of radiative transfer by the window. (The emittance of glass is $E_T = 0.84$; also, many plastics have high emittance values.) In certain cases a double-glazed window with a heat-mirror coating applied to an inner surface facing the air gap can perform thermally as well as a triple-glazed window.

Examples of double- and triple-glazed windows with heat mirrors are shown in Figure 2. One design depicts a heat-mirror coating on plastic. Deposition of heat mirrors on glass and plastic substrates is important. One fits well into conventional glass coating processes; the other is a refined extension of the metallizing process for plastics.

A heating-load heat mirror could also be used for solar thermal collectors as an alternative to a selective absorber. In this case, however, the heat mirror could be used with a nonselective absorber. One modification of this heat mirror is to shorten the transition or cut-off reflectance wavelength, as would be more suitable for the higher operating temperatures of solar collectors. The results of using a heat-mirror coating on a double-glazed flat-plate collector are shown in Figure 3. Also shown for comparison is the effect of using a selective absorber or antireflective coating.⁴ These coatings will be discussed later.

Transparent conductors for heat mirrors can be physically vapor deposited (PVD) on glass and plastic substrates by vacuum evaporative and sputtering techniques. Deposition on plastic tends to be more difficult than on glass because of the poor temperature durability of plastic. Window glass, on the other hand, can suffer from alkali-leaching reactions at elevated temperatures. Deposition methods, including chemical vapor deposition (CVD) and thermal polycondensation of organometallics, have been limited mostly to glass. The thermal and chemical stability of the substrate are significant in determining the proper deposition technique and conditions. Operational thermal durability and stability of substrate and coating are mandatory for long-life windows. Unfortunately, with heat-mirror coatings performance and durability commonly are inversely related.

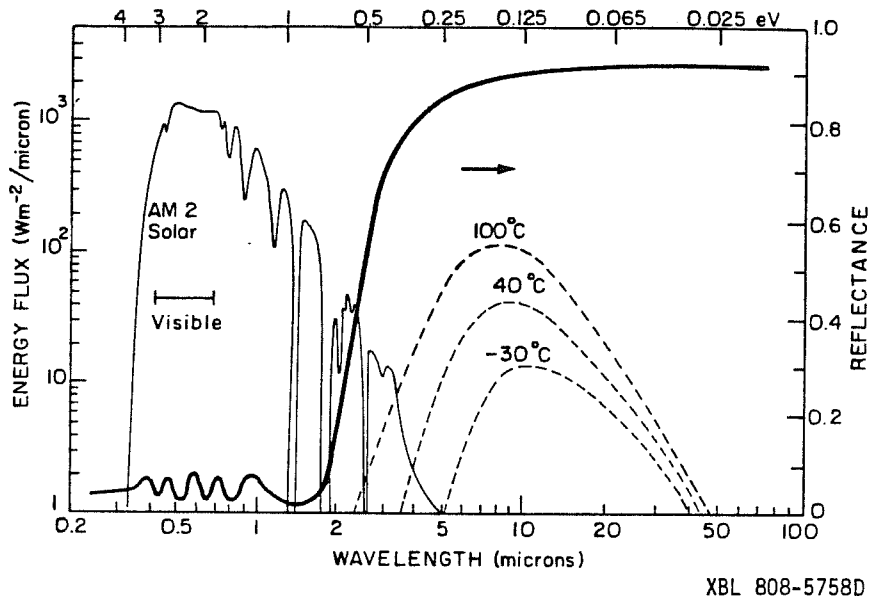


Figure 1. Spectrum of solar radiation (air mass 2) shown with three blackbody spectral distributions (-30°C , 40°C , 100°C). Superimposed is the idealized selective reflectance of a doped SnO_2 heat-mirror coating. The transmission spectrum is essentially the inverse of the reflectance.

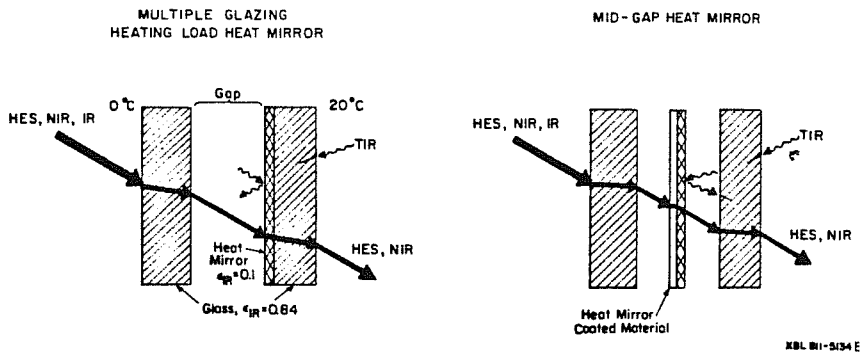
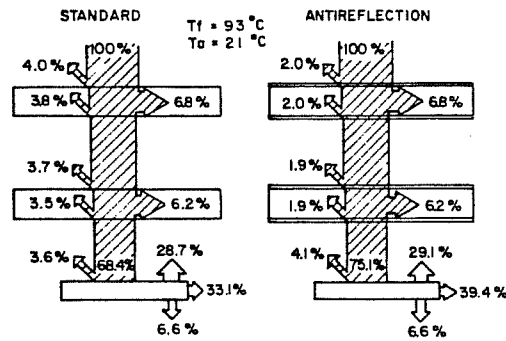
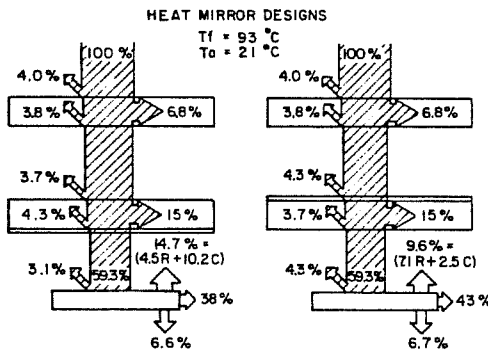


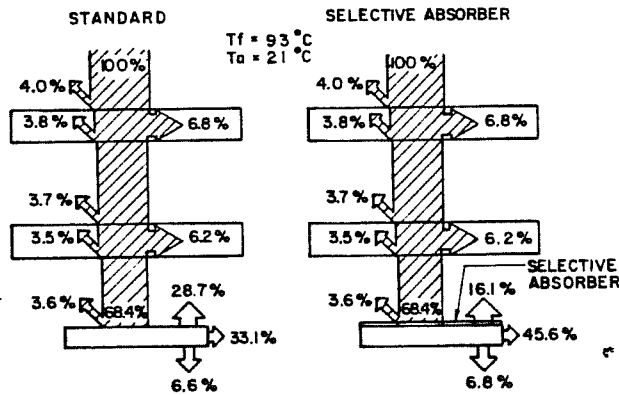
Figure 2. Two multiple-glazed windows incorporating heat mirrors. Both configurations have properties of high solar transmittance, low infrared emittance, and high infrared reflectance.



(a)



(b)



(c)

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Figure 3. The effect of various coatings on collection efficiency (T_f) for a flat-plate collector operating at 93°C (200°F) with ambient temperature (T_a) of 21°C (70°F). (a) Standard flat-plate collector compared to one with antireflective coatings. (b) Two placements for heat mirrors. (c) Standard flat-plate collector shown in contrast to one with selective absorbers. Notation: (R) stands for reflection, (c) for convection losses.³⁹

Doped semiconductor films. Heat-mirror films can be placed in two categories: multilayer dielectric/metal based films such as $\text{Al}_2\text{O}_3/\text{Ag}$, $\text{ZnS}/\text{Cu}/\text{ZnS}$, and $\text{TiO}_2/\text{Ag}/\text{TiO}_2$; and single-layer semiconductors (highly doped) such as $\text{In}_2\text{O}_3:\text{Sn}$ and $\text{SnO}_2:\text{F}$. There is growing interest in both multilayer and semiconductor heat mirrors in America, Europe, and Asia. Further information on heat mirrors is contained in a number of works.^{1,3}

Certain doped semiconductors exhibit high infrared reflectance due to the proper combination of high mobility ($>10 \text{ cm}^2/\text{V sec}$), carrier concentration (10^{20} to 10^{23}), effective mass, and lattice relaxation frequency. Material science details are outlined elsewhere.⁵ The best representative transparent semiconductors are $\text{SnO}_2:\text{F}$, $\text{SnO}_2:\text{Sb}$, $\text{In}_2\text{O}_3:\text{Sn}$, and Cd_2SnO_4 . Characteristic spectral transmittance and reflectance are presented in Figure 6 for some of the best laboratory-grade films on glass. The surface microstructure of a $\text{SnO}_2:\text{F}$ film is shown in Figure 6b. The transmission of these films can be increased by etching microgrids in the coatings.⁶ Techniques for depositing these coatings on polymeric substrates need to be improved. Table 1 lists the physical properties of selected doped semiconductor films. Detailed information on deposition process is enumerated elsewhere.^{1,5}

Table 1. Semiconductor Heat Mirrors⁴

Material	$\text{SnO}_2:\text{F}$	Cd_2SnO_4	$\text{In}_2\text{O}_3:\text{Sn}$	$\text{In}_2\text{O}_3:\text{Sn}$	$\text{Cd}_2\text{SnO}_4/\text{PET}$	$\text{In}_2\text{O}_3/\text{PET}$	$\text{In}_2\text{O}_3:\text{Sn}/\text{PET}$
Deposition tech.	Spray Hydro. 500-570°C	RF Sputt. Anneal 420°C	Spray Hydro.	RF Sputt. etched microgrid	REACT DC Sputt. & RF BIAS	REACT DC Sputt. & RF BIAS	REACT RF Sputt.
Sheet Resist. (ohm/sq)	4	26-43	15-20	3	24	30	<30
Thickness (microns)	1.0	< 0.3	-	0.35	0.28	0.34	0.5
Mobility ($\text{cm}^2/\text{V-sec}$)	37	-	-	-	30	29	-
Carrier Density ($\text{cm}^{-3} \times 10^{20}$)	4.4	-	15	-	3.4	2.1	-
T_{vis} (ave) or (T_g)	(0.75)	(0.86)	-0.9	(0.90, AM2)	-0.65	-0.78	0.8
R_{ir} or (E_{ir})	(0.15)	(0.12, 77°C)	0.85	0.83, 10um	0.7, 10um	0.7, 10um	0.8, 10um
Reference	46	45	44	6	56	56	43

There are other promising heat-mirror materials, including some of the rare earth oxides and borides, transition metal nitrides and carbides, and selected ternary systems. Although little knowledge has been obtained optically about these materials, they are known to exhibit Drude-like electrical conduction. Also, graded refractive index and surface-textured heat-mirror coatings are yet to be developed. Compared with current films, they show promise of improved solar transmission.

Multilayer heat-mirror films. Metal films less than approximately 100 angstroms thick exhibit partial visible and solar transparency. Properly chosen dielectric coatings protect and partly antireflect the metal film in the visible region, thereby increasing light transmission. When used to overcoat a metal, the dielectric film must exhibit high infrared transmittance in order to preserve the infrared reflectance of the metal. Generally, further protection is required of the metal/dielectric films because they are quite thin and vulnerable to atmospheric corrosion and abrasion. Determination of the appropriate dielectric type and thickness is discussed elsewhere.⁷ Example systems¹ are polymer/M, $\text{Al}_2\text{O}_3/\text{M}$, SiO_2/M , $\text{TiO}_2/\text{M}/\text{TiO}_2$, $\text{ZnO}/\text{M}/\text{ZnO}$, and $\text{ZnS}/\text{M}/\text{ZnS}$ where M is a metal such as Ag, Al, Au, Cr, Cu, Ni, or Ti. Additional designs include X/M and X/M/X where X is an appropriate semiconductor or polymer. Infrared-transparent polymers of polyethylene, polyvinylidene chloride, polyacrylonitrile, polypropylene, and polyvinyl fluoride might be used for this application. Their broad wavelength tunability gives multilayer films an advantage over the doped semiconductors. Some properties of selected multilayer films on glass and plastic substrates are shown in Figures 4 and 5. Detailed data on the properties of these films are shown in Table 2. Extensive data on D/M/D coatings are covered elsewhere.¹ Improving the durability of multilayer films remains a critical research area for the materials scientist.

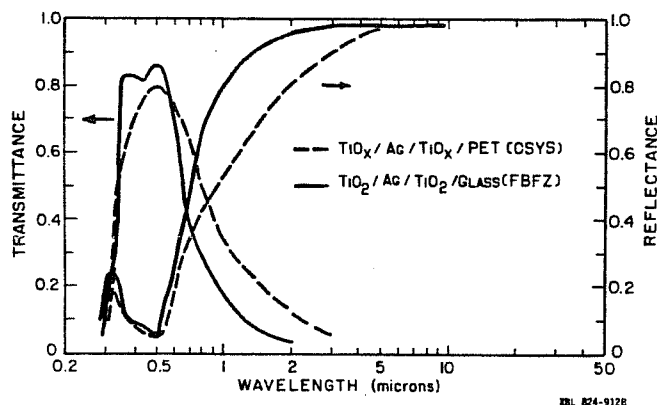


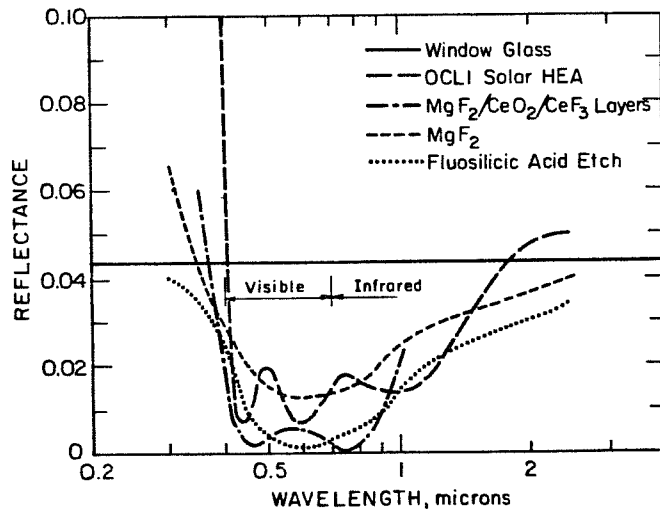
Figure 4. $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ coating on glass⁴⁰ and polyethylene terephthalate (PET).⁴¹

Table 2. Multilayer Heat-Mirror Films⁴

Material	Al ₂ O ₃ /Ag	TiO ₂ /Au/PET	TiO ₂ /Ag/TiO ₂	TiO _x /Ag/TiO _x	ZnS/Ag/ZnS
Deposition tech.	Ion Beam Sputt.	e-Beam Evap. & Chemical Dep.	RF Sputter	Chemical Dep. & Vac Evap.	Vac. Evap.
Sheet Resist. (ohm/sq)	-	10	-	-	10
Thickness (angstroms)	-	-	180/180/180	270/150/270	520/100/770
T _{vis} (ave) or T _s	0.47, 0.5um	0.80	0.84	-0.75	0.68
R _{ir} or (E _{ir})	0.93, 2.5um	0.87	0.99, 10um	0.98, 5um	(0.06)
Reference	57	58	40	59	60

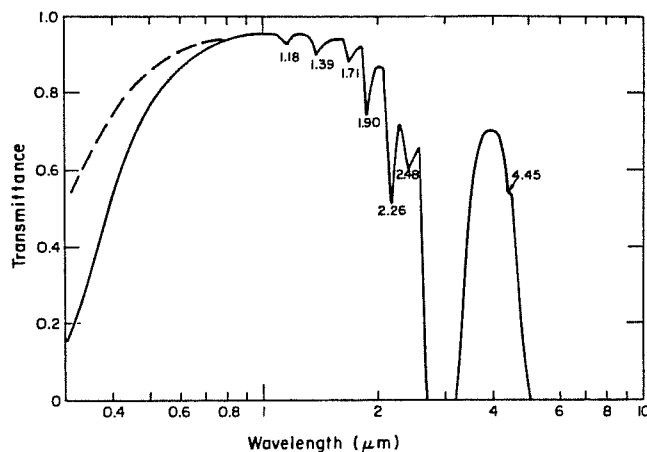
High-transmittance antireflective films

Antireflective coatings, if the proper materials are used, can also serve as durable overcoating materials. For photovoltaics, some polymeric and elastomeric protective coatings can be effective antireflective materials if the coating is thin enough, although protective coatings are generally used in thick-film form. Popular protective materials are silicones, fluorocarbons, halocarbons, and acrylic resins. One major need is to develop a coating that serves both protective and antireflective functions. Some polymers having a low refractive index (n) can antireflect glass ($n = 1.5$) and high-index plastics. Dispersions of fluorinated ethylene propylene ($n = 1.34$) can be used for this purpose. Polyvinyl fluoride ($n = 1.46$) can be antireflected by dipping in acetophenone. Graded-index films present a versatile range of coatings having refractive indices that are not readily found. As compared to other films, fluorosilicic acid can give a graded-index, antireflective coating to glass (see Figure 7). It primarily roughens the surface by etching out small pores in nonsilica regions.^{8,9} Silica films deposited from sodium silicate or colloidal silica can be used for acrylic, polycarbonate, and several glasses. A treatment has been devised for polyethylene terephthalate (polyester) and glass materials.^{10, 11} The coating is made from a steam-oxidized aluminum film; this processing produces a needle-like structure of aluminum hydroxide [AlO(OH)], as shown in Figure 8. A polyester film treated in this fashion can serve in glazing applications where solar transmission must be maximized (see Figure 9). Inorganic thin films have been used for a wide range of single- and multiple-interference coatings. Compounds such as MgF₂, CeO₂, CeF₃, SiO, SiO₂, and TiO₂ have been used in various combinations for antireflection applications. In addition to the traditional PVD techniques, a number of oxides can be dip-coated onto optical substrates. Coatings of hot hydrolized metal alkoxides can be polycondensed, forming oxides of transition metals, refractory metals, and some rare earths.¹² A similar technique known as the sol-gel process has produced mixed TiO₂-SiO₂ antireflective films on silicon¹³ and black chrome. Diamond-like (i-carbon) transparent coatings have been used for antireflective films. They are formed from plasma decomposition of hydrocarbons and ion beam depositions.¹⁴ Coatings of about $n = 1.9$ can be made which are suited to photovoltaics. However, the absorption of i-carbon films must be reduced before they can be utilized for optical applications.



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Figure 7. Reflectance for various antireflection treatments for glass.²

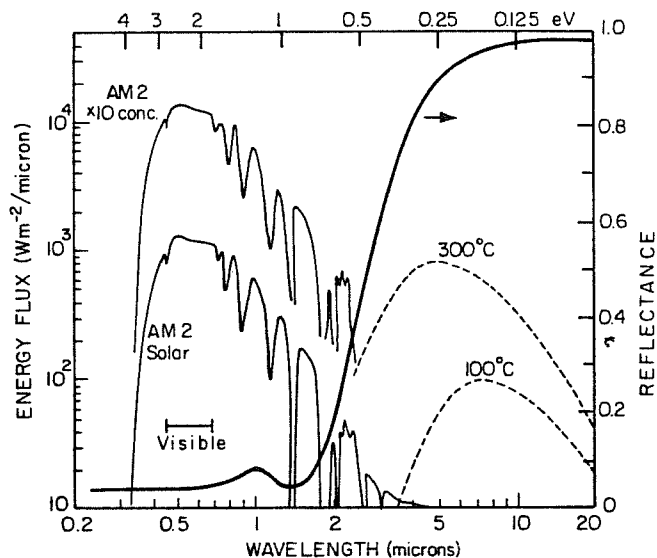


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Figure 11. Spectral normal-normal transmittance (solid line) and spectral normal-hemispherical transmittance (dashed line) of silica aerogel 4mm thick.¹⁵

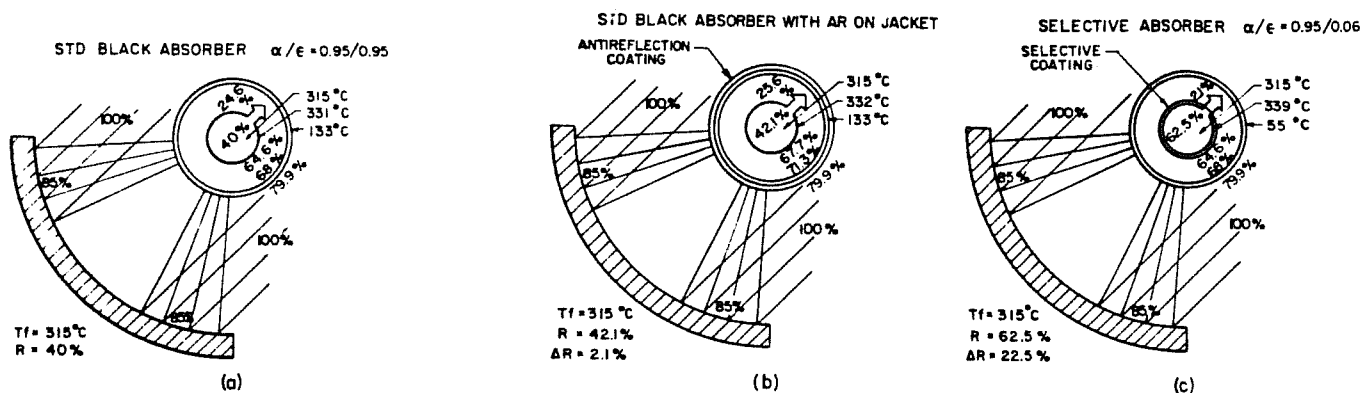
Solar absorbers

There are two categories of solar absorbers for collectors, selective and nonselective. The selective absorber has optical properties that vary greatly from one spectral region to another. The selective absorber or selective surface efficiently captures solar energy in the high-intensity visible and the near-infrared spectral regions while exhibiting poor infrared radiating properties. This characteristic is depicted in Figure 12. In contrast, a nonselective absorber such as ordinary black paint has a flat spectral response and loses much of its absorbed energy reradiation. The optimum characteristics of a solar absorber are high solar absorptance and minimum emittance (or maximum reflectance) in the infrared. The exact transition wavelength is determined by the chosen application, solar concentration, and operating temperatures. Examples of concentrating collector designs are shown in Figure 13. Solar selectivity can be obtained by a variety of methods, including semiconductor/reflector tandems, composite coatings, multilayer thin films, and optical trapping surfaces. Also intrinsic materials and films with quantum size effects can exhibit wavelength selectivity. Significant reviews have been written about solar absorbers, giving insight and detail beyond the scope of this work.¹⁶⁻²⁰ A selected group of solar selective absorbers is outlined in Table 3.



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Figure 12. Wavelength relationship between a characteristic black chrome solar selective surface in terms of reflectance to that of solar energy (air mass 2) and blackbody spectra (100°C, 300°C).



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Figure 13. The effect of various coatings on collection efficiency for a parabolic concentrating evacuated collector operating at 315°C (600°F) with ambient temperature of 21°C (70°F). (a) Non-selective black coating. (b) Non-selective black coating with antireflection coatings. (c) Selective coatings. Notation: (R) stands for net collection efficiency, (ΔR) change in collection efficiency over that of a standard black absorber.³⁹

Table 3. Properties of Selective Absorbers

Absorber ¹	Type	Deposition Technique	Maturity ²	A_s	E(°C)	Stability ³ (°C)	Estimated Commercial Cost (US\$/ft ²) ⁴	Ref.
Copper	Textured	Sputter etch	1	.9-.95	.08-.11	300(air)		35
SS	Textured	Sputter etch	1	.9-.96	.22-.26	350(air)		35
Ni	Textured	Sputter etch	1	.9-.95	.08-.11 (27)	250(air)		35
ZrB ₂ /Si ₃ N ₄	Intrinsic	CVD	1	.93	.08-.09 (102)	500(air)		61
Cr-Cr ₂ O ₃ (black chrome)	Graded Composite	Electro-plating	5	.92-.97	.04-.06 (100)	400(air)	coating:0.85 foil:1.50	50, 62,63
Cr-Mo-Cr ₂ O ₃	Graded Composite	Co-electro-plating	1	.96-.97		400(air)	> black chrome	64
Ni-Al ₂ O ₃ /Al ₂ O ₃	Graded Composite	Anodic Oxidation	5	.92-.97	.1-.26 (65)	300(air)		34
Zn-ZnO	Graded Composite	Anodic Oxidation	1	.98	.18(100)	<300(air)		65
Cu ₂ O-CuO-Cu	Composite/Tandem	Anodic Oxidation	1	.95	.34(100)	130(air)	.25	66
NiO-Ni-Cr/NiCrO _x	Graded Composite	Chemical Conversion	5	.97-.99	.07-.1 (100)	250(air)	foil:1.80	27,29
SS-C	Graded Composite	Reactive Magnetron Sputtering	3	.94	.03-.1 (100)	300(vacuum) 200(air)	.5	67
SS-C (on rough sputtered copper)	Textured Composite	Reactive Mag.Sput.	3	.9	.04(67)	450 (vacuum)	.5	68
SS-SSO _x /SSO _x	Anti-Ref. Composite	Reactive Mag. Sput.	1	.89-.93	.08(20)	150(air)		69
Cr-Al ₂ O ₃	Graded Composite	Dual Source Mag. Sput.	1	.92	.09(20)			69
Mo-MoO ₂ /Si ₃ N ₄	Composite/Intrinsic	CVD	1	.91	.11(500)	500(vacuum) 300 (air)		70
Tellurium	Textured Tandem	Angled Vapor Deposition	1	.92	.03			71
a-Si/Si ₃ N ₄	AR Tandem	CVD	1	.75	.08(500)	500(air)		72

Table 3. Properties of Selective Absorbers cont'd.

Absorber ¹	Type	Deposition Technique	Maturity ²	A _s	E(°C)	Stability ³ (°C)	Estimated Commercial Cost (US\$/ft ²) ⁴	Ref.
Cu ₂ S	Tandem	Chemical Spray Dep'n	1	.89	.25(100)	130 (air)	.25	73
CoO	Textured Grd'd Tand.	Electropl'd Co: 1 Heat Oxd'n		.98	.2(100)	425(air)		74
CoO-FeO ₃ -Co ₃ O ₄	Textured Tandem	Electropl'd Co: 1 Heat Oxd'n		.9	.07(100)	300(air)		75
Ge-CaF ₂	Semicon.in a Dielec.	Sputtering	1	.65-.72	.01-.1 (100)			76
Ge	Textured Tandem	Rf Sputt. H ₂ O ₂ etching	1	.98-.99	.58			77
AMA (M=Cr)	3-layer	Re.Mag.Sput.	3	.95	.12(20)	300(air)	.2-.5	78
AMA (M=Ni)	3-layer	Re.Mag.Sput.	3	.91	.08(20)	350(air)	.2-.5	78
AMA (M=Ta)	3-layer	Re.Mag.Sput.	3	.89	.12(20)	300(air)	.2-.5	78
Proprietary	3-layer	Elect.B. Evap.	3	.92-.96	.05-.08	250(air)	foil: .7-.8	17
Al ₂ O ₃ /Pt-Al ₂ O ₃ /Al ₂ O ₃	3-layer Composite	Rf Mag. Sput.	3	.91-.93	.08-.1 (20)	>600(air)	1 (on Cr)	78
Al ₂ O ₃ /Mo-Al ₂ O ₃	Composite	Co evap.	1	.99	0.2(500) 0.08(200)	750(vac)		79
ZrC _x /Zr	Tandem	RF Sputt.	3	.93	0.25	625 (vac)		28
Cr-CrO _x	Composite on Al foil	react. evap.	3	.9	0.05	175		28
Ni-C	Composite	Sputtering	1	.8	0.028-0.035 (150)			80
NiN _x	Tandem	Sputtering	1	.84	0.039 (150)			80

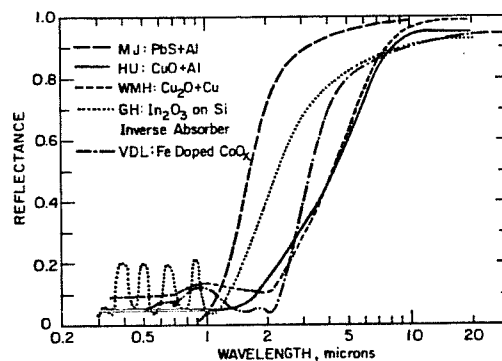
Notes: ¹ Absorber layers are separated by a/. Constituents of composite layers are separated by a -.

² Maturity of absorber coatings: 5 commercial, 3 development, 1 research.

^{3,4} Temperature stability and commercial cost for most absorbers are not well known. Costs are in US \$ (1981).

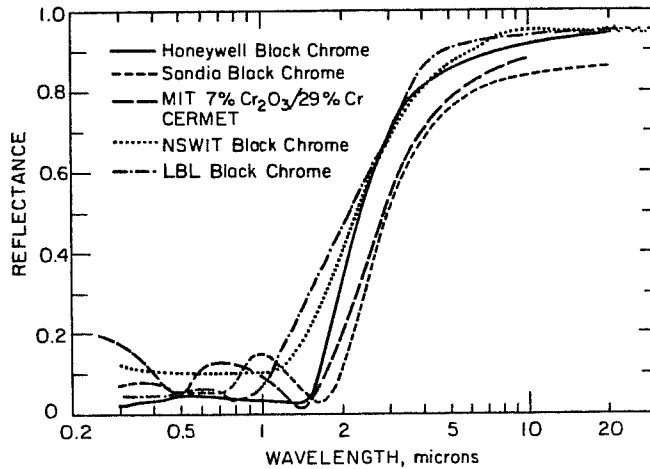
Semiconductor/metal tandems

Semiconductors coated with metals provide complementary functions as spectrally selective surfaces. The semiconductor provides high absorptance in the high-energy solar region and becomes transparent beyond its absorption edge in the infrared. In the infrared, the underlying metal layer gives the tandem or metallic reflectance as low emittance. A simple tandem is an oxidized metal. Usually, the natural thickness of an oxide is not optimum or is not stable in operation. Many chemical conversion processes are used to oxidize metals such as stainless steel, copper, and titanium. Other tandems can be made with deposits of oxides on a variety of metals.² Examples are shown in Figure 14. High-temperature absorbers can also be designed such as the Si/Ag absorber, which is stable to 500°C.¹⁸ Tandem absorbers can be fabricated by simple chemical conversion or electrochemical, CVD, and PVD (sputtering and evaporation) processes. Composite coatings can also be used as the absorber portion of tandem absorbers.



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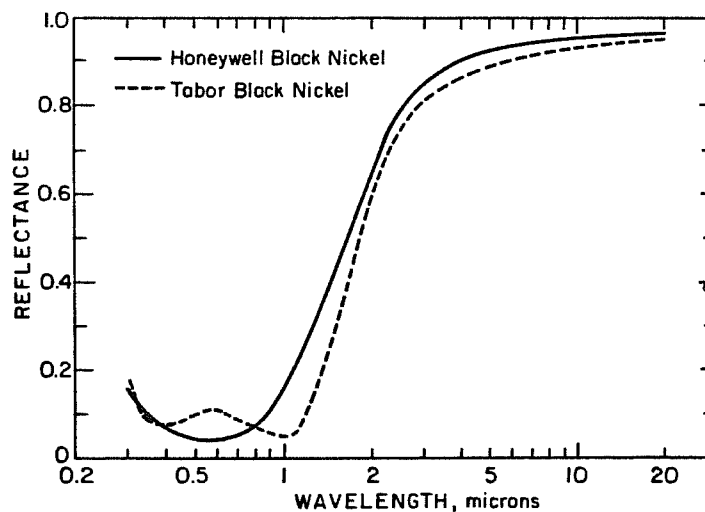
Figure 14. Reflectance of various tandem absorbers: PbS/Al⁴⁷, CuO/Al, Cu₂O/Cu⁴⁹, and CoO_x/Fe/Ni.⁴⁶



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Figure 16. Reflectance for different types of selective black chrome absorbers.^{2,51,52}

Electrodeposition of black nickel produces a very interesting structure. By changing plating parameters during deposition, layers of ZnS and NiS can be formed on top of a metallic substrate. This absorber shows a combination of tandem and multilayer interference. The reflectance for the two varieties is shown in Figure 17. Multilayer effects will be discussed later. It is important to note that sometimes combining effects in a single absorber may make a superior, although more complicated, design.



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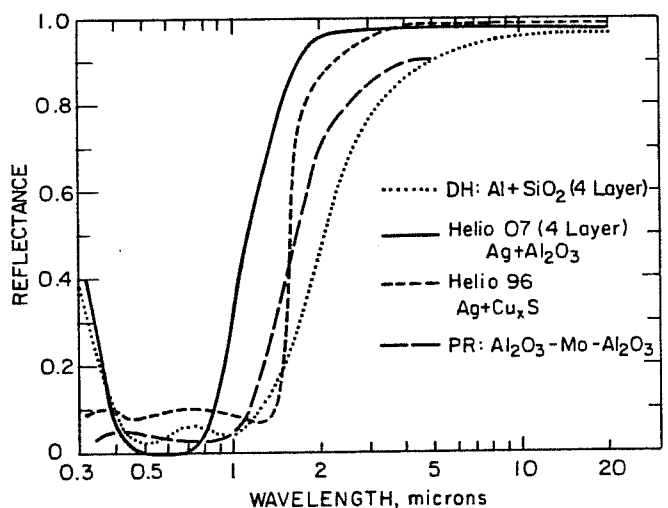
Figure 17. Spectral reflectance for black nickel.^{53,54}

The Quantum Size Effects (QSE)³⁰ theory regarding tandem absorbers is of interest. QSE occurs in thin films of metals, perhaps less than 10-100 angstroms for metal and 400 angstroms for degenerate semiconductors. QSE relates the influence of the geometrical dimensions of the sample to the distribution of electron states. This distribution can be optimized by size effects to interact strongly with incident electromagnetic radiation. A combination of a QSE material and a reflective metal layer can produce in a tandem absorber. QSE has been experimentally verified for InSb/Al, and InSb/Ag.³⁰

Two effective medium theories that can be used to describe composite solar absorbers are Maxwell-Garnett Theory and Bruggeman Theory.^{31,32}

Multilayer absorbers

Multilayer thin films make excellent solar absorbers. Dielectric/metal/dielectric combinations known as interference stacks behave like selective filters for energy absorption. The desired operation of an interference stack is to capture energy between metal-dielectric alternations. Specific solar wavelengths are absorbed by multiple reflections in the layers. Wavelengths that are not of the absorption, or tuning, frequency of the multilayer films are reflected. For solar energy absorption, a broadband filter is required. Thin-film responses are shown in Figure 18. The disadvantage of most multilayer coatings is that they are fairly expensive to fabricate compared to a single-layer coating. These coatings can also suffer from interdiffusion and corrosion at elevated temperature and humidity. In spite of all this, stable multilayer coatings exist, such as the $\text{Al}_2\text{O}_3/\text{Mo}/\text{Al}_2\text{O}_3$ design.³³ The metal layer in these coatings is typically 50-100 angstrom thick, appearing semi-transparent to incoming radiation. The dielectric layers need not be intrinsically absorbing to solar radiation because this three-layer structure behaves as a resonant cavity tuned to a band of solar wavelengths. A novel graded-layer coating has been devised by dc anodization of aluminum.³⁴ The coating is made by phosphoric acid anodization followed by an ac electrolysis of a nickel-pigmenting bath. The structure of this coating consists of porous Al_2O_3 in which the lower portion of the pores is filled with bundles of needle-shaped nickel particles. A thin Al_2O_3 barrier layer protects the aluminum substrate.



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Figure 18. Reflectance for example multilayer absorbers of the dielectric/metal type. Also included is the Al_2O_3 -Mo- Al_2O_3 high-temperature absorber.⁵⁵

Optical trapping surfaces

It is possible to roughen surfaces so they will enhance absorption geometrically in one wavelength region but appear smooth in another. This technique is possible because the wavelength of the high-energy solar spectrum is distributed far enough away from the thermal infrared spectra. Materials can be grown as dendrites or rough crystallites, or can be surface-roughened to form optical trapping surfaces as in Figure 19. These dendritic materials do not require a high intrinsic absorption as they rely on multiple reflection and partial absorption to give a large effective absorption. Materials such as NiAl_x , W, Mo, Ni, Cu, Fe, Co, Mn, Sb, and stainless steel have been grown as dendrites or textured by sputter etching.^{2,35,36} Texturing of surfaces is also an excellent method to make other types of absorbers and reflectors, as has been done with great success with the Mo- Al_2O_3 composite absorber.³⁷

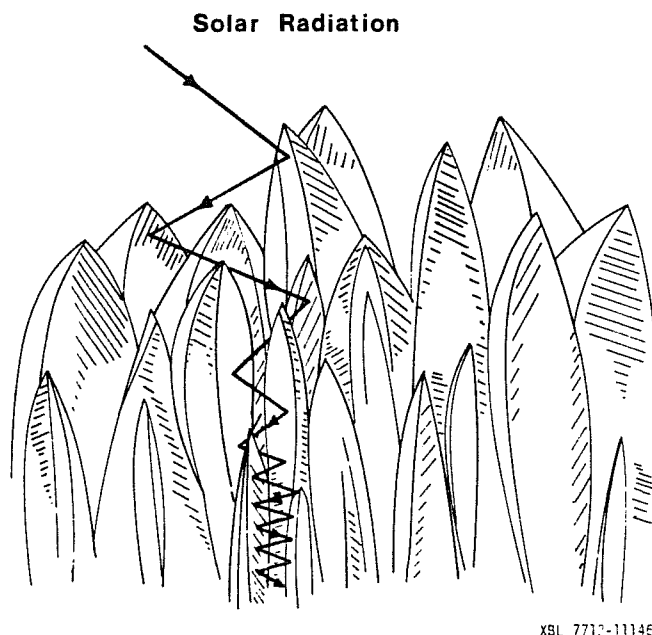


Figure 19. Schematic of dendritic absorber surface.² The dendrites are highly absorbing in the visible region due to multiple trapping. In the infrared (longer wavelength) they appear smooth.

Absorber paints

If a thermally resistant, property-stable paint could be developed which offered the solar selectivity of black chrome at a low cost, the solar coating industry would be revolutionized. No highly selective paint yet exists. There are a few that exhibit partial solar selectivity and are commercially available. Others, however, are still in the research stage. A number of nonselective paints are listed elsewhere.² Three approaches can be taken in designing a selective paint. One makes the paint coating very thin so that the low-infrared emittance of the metal substrate dominates the infrared. Notice that a metal substrate is specified. For passive applications such as Trombe walls the substrate would probably be concrete or brick, in which case this type of paint would not be selective. The major problem with thickness-sensitive paints is that their binder material, usually a polymer, exhibits dominant infrared absorption bands. This absorption increases the infrared emittance of the paint. To remedy this either a special polymer must be devised or an inorganic system must be used. Another approach to the paint is to incorporate a coated metal flake. In this way the selective effect is created as a distributed tandem, with each particle serving as an individual tandem absorber; recent research has documented this effect³⁸. A third approach is to use an intrinsic absorber material such as ZrB_2 and disperse it in a low-absorbing binder. The final solution relies on development of both the intrinsic absorber and binder. A few properties of selective absorber paints are detailed in Table 4.

Table 4. Selective Absorber Paints

All data taken from manufacturers' product literature or research reports; accuracy or completeness has not been verified.

Type	Highest Operating Temp. in Air	$A_s(T), \epsilon_{ir}(T)$	Ref.
Soot/polyurethane alkyd	>70-100°C	0.90, 0.30 (100°C)	81
Thermalox Silicone-based	537°C	0.96, 0.52 (84°C)	2
Solkote-Hi/Sorb	880°C	0.95, 0.44	2
Fe, Mn, Cu oxides + silicone	200°C	0.9, 0.31 (100°C)	38
Fe, Mn, Cu oxides + silicone epoxy	200°C	0.9, 0.31 (100°C)	38
Fe, Mn, Cu oxides +* /Al flake and silicone	>600°C	0.91-0.93, 0.8-0.1 (20°C)	38

*Thickness-insensitive

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